

Spatial Distribution of Trap Levels in $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$

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Abstract

The current-voltage cycling effect (electric conditioning) is investigated using the complex impedance spectra of the perovskite poly-crystals $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$. Some of the Cole-Cole semicircles respond strongly to the electric conditioning process, others do not. Under the assumption that the main dielectric response is always due to the same trap state, the different electric field sensitivities can only be explained by different trap environments in the different boundaries. We think that there is a long range polaronic selftrapping effect of the trap charges, which produces a deeper energy level at the surface.

Keywords

Impedance Spectra; Trap States; Selftrapping Effect

Introduction

The colossal dielectric constant (up to 10^5) material $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) has aroused wide spread interest and investigations in recent years, as its high dielectric constant is nearly constant within a wide temperature and frequency range, but with no phase transition or structural change [Sinclair et al 2002, Homes et al 2003]. For the focused development of applications the origin of these unusual dielectric properties should be addressed. Polycrystalline CCTO was shown to have semiconducting grains and insulating grain boundaries based on Scanning Probe Microscopy measurements and impedance spectra; thus a grain boundary BLC (barrier layer capacitance) model has been widely accepted as the origin of the high permittivity [Chung et al 2004, Fiorenza et al 2011, Fang et al 2005]. But it is always in argument that which kind of boundaries contribute largely to the BLC. Some authors think that the high values of the dielectric constant of CCTO are due to electrode polarization effects [Lunkenheimer et al 2002, Lunkenheimer et al 2004, Cao et al. 2007]. Some believe that the inner boundaries such as grain boundaries or domain boundary polarization play the important role. [Adams et al 2006, Li et al 2006]. However, in single crystal CCTO samples, which also have large dielectric constants, the contribution of inner domain boundaries is plausible [Ahlawat et al 2013, Zheng et al 2010]. In this work, we tried to resolve disputes about which region contribute to the dielectric response mostly, and find out the true reason of the polarization.

Impedance spectroscopy is one of the few methods which considers the spatial distribution of space charge layers or defect clusters at the boundaries. Usually, in ceramic materials, one finds several semicircles in the complex impedance plane which can be equivalent to a R-C (resistance – capacitance) parallel elements. The location and height of the semicircles gives some insight into the distribution of the charged defects. In CCTO several investigations have shown that there are up to three semicircles [Bärner et al 2011, Shao et al 2006]. In this work we find that the third, high resistive semicircle is very sensitive to the applied external field. The field sensitivity plus the location of the third semicircle in the complex plane has led to a tentative assignment to surface space charge layers which are easy to manipulate by external electrical fields.

Experimental

CCTO ceramics were synthesized using the traditional solid state reaction method, i.e. analytically pure raw

materials of CaCO_3 (99.99%), CuO (99%), and TiO_2 (99.5%) are mixed and presintered. Details can be found in reference [Luo et al 2010]. The finally dense discs were of a diameter of 10 mm, and thickness of about 1.5 mm, which were sintered at 1100°C for 12 h in air. On-sintered silver paste (580 °C for 10 min) was used to coat both sides of the disks, thus serving as electrodes. The impedance spectra were measured in the frequency range of 20 Hz–3 MHz at 420 K, using a WK6420 impedance analyzer together with a Janis closed-cycle-refrigerator. The electric conditioning (EC) was performed using a commercial electrometer Keithley 2400 under a computer-controlled program. EC means that the sample undergoes repeatedly a continuous voltage sweep scanning between ($0 \rightarrow +V_{\text{max}} \rightarrow 0 \rightarrow -V_{\text{max}}$), applied to the electrodes, and simultaneously, one monitors the variation of the current. The body resistance and surface resistance were detected by Keithley 6517 at room temperature, and the connection methods for the measurement of body and surface resistance were obtained in the instrument of the Keithley6517.

Results

Cole-Cole Semicircles under Electric Conditioning

In previous work [Bärner et al 2011] on CCTO we had observed three semicircles which change position in the complex plane at different temperatures. There are two semicircles with a non-zero intercept at 420 K. The semicircle at the lowest frequency we call semicircle III. The semicircle at middle frequencies we call semicircle II. Besides the two semicircles, at high frequency there is a non-zero intercept which will disappear and develop another semicircle with zero intercept at low temperatures, say at 80 K, we call it semicircle I [Bärner et al 2011]. However, which region of the sample can be assigned to a specific semicircle is always in argument. In order to narrow down the possibilities, we investigated the change of the semicircles under electrical condition (EC). As shown in Fig. 1, at first the I - V (current – voltage) curves are hysteretic with a lower slope, and after several EC cycles, the overall I - V (current – voltage) characteristic of CCTO will become almost linear. If then we remove the dc voltage (operation time 3 s) and measure the recovery of the resistance, the resistance of the sample will gradually increase (inset (b)) and the capacitance will go through a peak (recovery process) then recover to the values before EC (inset (a)) [Luo et al 2011]. The abnormal behaviours of resistance and capacitance after EC were proved to be reversible that it will happen during EC [Luo et al 2011]. It suggests that there might be trap charges relaxation in the process of boundary space charge layer depletion.

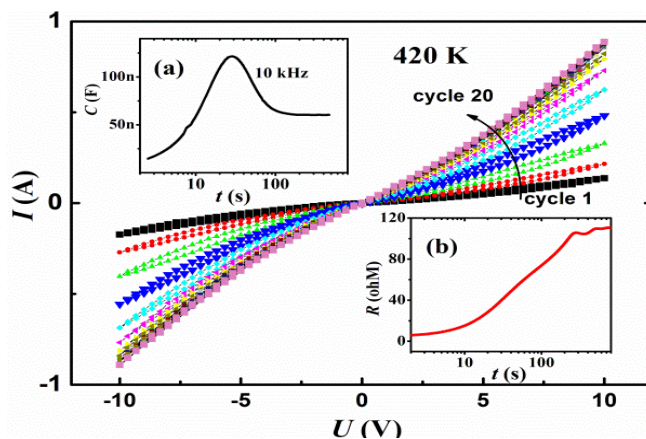


FIG. 1 THE I - V CYCLES (ELECTRIC CONDITIONING) PROCESS AT 420 K, INSET SHOWS CAPACITANCE (INSET (A)) AND RESISTANCE (INSET (B)) CHANGES WITH RECOVERY TIME.

The electric conditioning effect on the Cole-Cole semicircles is shown in Fig. 2. Here, we compare the Cole-Cole semicircle changes before, during and after electric conditioning. When we stop the EC at a certain I - V cycle, the sample response will stop at a certain state and then recover. As the full conditioning effect disappears in a time of about 2 minutes, and as a frequency sweep consumes almost the same time, we could not run over the full frequency spectrum at each stop but had to choose individual starting measuring frequencies in order to obtain reliable data. In order to observe the changes of the lowest frequency semicircle III, we choose a frequency of 120 Hz, as shown in Fig. 2 (a); to observe the change of the higher frequency semicircle II, we choose a frequency of 3×10^4 Hz and 8.6×10^4 Hz, as shown in Figs. 2 (b) and (c). It is found that if we choose 120 Hz for the starting

frequency, changes of the low frequency semicircle could be watched simultaneously with the appropriate I-V conditioning cycles. When we choose the start frequency 3×10^4 Hz or 8.6×10^4 Hz, both of which belong to semicircle II, only minor radius changes can be observed under voltage conditioning (see Fig. 2 (b) and Fig. 2 (c), insets are the magnified images). Thus, we can conclude that only semicircle III is sensitive to the electric conditioning.

Cole-Cole Semicircles after Mechanical Polish

In order to ascertain whether semicircle III represents the response of space charges at the surface or not, we changed the surface topological state of the sample using mechanical polishing, then repeating the impedance measurements. The experiments were taken at 420 K where both semicircle III and semicircle II can be observed. There is indeed a significant change of the response of the two semicircles, as shown in Fig. 3(a). At 420 K, semicircle III changes drastically after mechanical polishing, probably due to the mechanical stress which is introduced or taken away, changing the trap state energy levels. The high frequency semicircle suffered only minor changes; these small changes might indicate that the surface layer might extend into the bulk for a few grain sizes (a few μm). The results taken together suggests that semicircle III is indeed related to a surface space charge layer, but then the semicircle II has to be assigned to the inner grain boundary space charge layers. Indeed, if we measure the changes of surface and body resistance before and after mechanical polish respectively, the results are different. Before the polish, the surface resistance that shown as the reciprocal of the I-V curve, is about 10 times larger as the bulk resistance. After the polish, we see that the surface resistance has changed significantly (see Fig. 3(b)), while the bulk resistance has changed very little (see Fig. 3(c)). The insets of Figs. 3(b) and (c) sketch the methods of measurements of the surface and inner boundaries resistance, respectively. The results confirmed our speculation, however, at this point we still do not know why the surface space charge layer is so very sensitive to electric fields.

Discussion

The surface treatment experiments in connection with the Cole-Cole semicircles have shown that dielectric dispersion response probably has two spatially separated sources. It was proved that the intrinsic Schottky barrier at the boundaries is responsible for the nonlinear I-V characteristics [Chung et al 2004]. The two surfaces of the sample coated with silver mainly represent a back-to-back Schottky barrier in series and perpendicular to the electric field, as shown in Fig. 4 (a), the external electric field (E_{ext}) pass through the two surfaces directly. While the inner boundaries are both in series and parallel to the E_{ext} , the external field drops mostly across the surface layers and so only a small percentage of the applied voltage V is loaded on each inner grain boundary. This might be one reason why semicircle III is sensitive to electric conditioning, while semicircle II is insensitive. However, if it is only a Schottky barrier, the relaxation (emitting or retrapping electrons) is very fast that we only observe a reversible and non-linear I-V. That means that if the external electric field $E_{\text{ext}} \rightarrow 0$ and then changes sign (reverse cycle), we should reversibly recover the starting situation. But apparently the nonlinearity of the I-V curves changes with increasing voltage load cycles, which shows a slow relaxation process. Thus only a Schottky barrier is not enough to explain the slow electric transport.

In order to explain the resistive switching behaviour of $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$, Sawa et al had proposed an interface-state-induced band bending at the interface between electrode and sample, which also leads to a reversible nonlinear I-V curve [Sawa et al 2004]. In that scenario, the degree of band bending (the barrier height) depends on the density and the energetical distribution of the interface states. In CCTO, the non-linear I-V suggest a Sawa scenario, i.e. there is rather broad distribution of trap sites at the surface (interface). However, normally the Sawa scenario does introduce a stable resistive switching behavior and does not change under continuous I-V-load cycles. Moreover, in our case, the slow relaxation process which accompanies the slow change process from non-linearity to linearity, cannot be attributed to a normal Sawa scenario but rather suggests an interaction between the trap states at the surface. We think that the accompanying relaxation process could be an external field (E_{ext}) induced collective selftrapping [Bärner et al 2013].

As the external potential drop near the surface is strongest, the space charges would tend to accumulate at the surface if there are already vacant trap sites. With E_{ext} increasing, the accumulation will go on until the electrical field becomes that high that only Frenkel-Poole type emission would stop the accumulation process. Such effects

are called “selftrapping”, which have already been proposed and observed in manganites. In particular for LaMnO₃ a rather large static spin-polaron cloud that is capable of deepening a hole trap level was proposed [Gennes 1960]. This would be a case of selftrapping under magnetic polarisation, i.e. in the magnetically ordered state which is susceptible to an applied magnetic field \vec{H} via the Zeeman term $\vec{M} \cdot \vec{H}$ [Zock et al 1995]. Similarly, in CCTO there may be different electric polarization regions, such as the space charges layers at the grain boundaries or at the surface, which are also susceptible to an electrical field via the analog dipole energy $\vec{P} \cdot \vec{E}$, eventually leading to internal field deepened trap levels in CCTO.

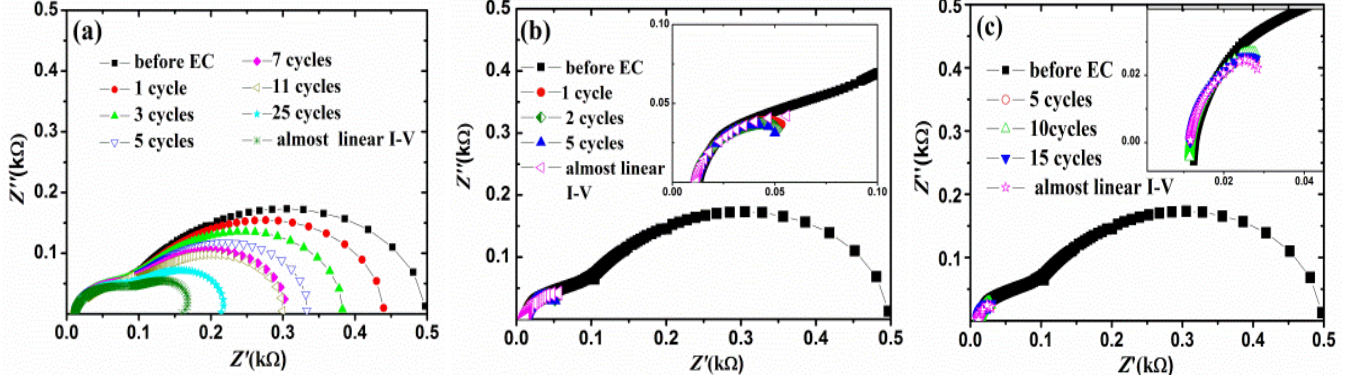


FIG. 2 THE CHANGES OF SEMICIRCLE AT DIFFERENT ELECTRIC CONDITIONING PROCESSES AT 420 K. THE STARTING MEASURING FREQUENCIES ARE (A) 120 HZ, (B) 3×10^4 HZ AND (C) 8.6×10^4 HZ.

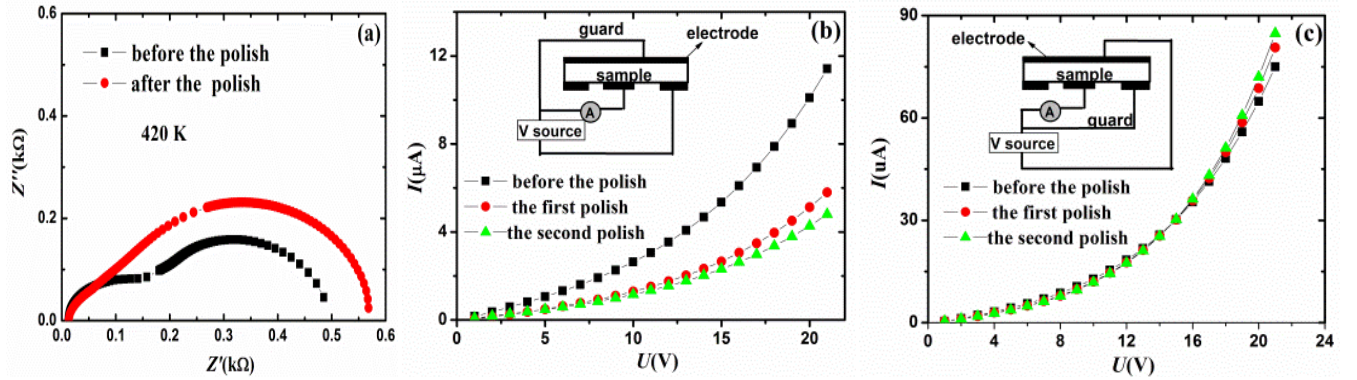


FIG.3 (A) THE SEMICIRCLE RESPONSES AT 420 K BEFORE AND AFTER MECHANICAL POLISH. (B) AND (C) ARE THE I-V CURVES MEASURED BEFORE AND AFTER POLISH FOR THE VOLTAGE APPLIED ACCROSS SURFACE AND BODY RESPECTIVELY.

In the process of selftrapping, the trap states dig in (go lower beyond linearity) and therefore are only relatively releasing (retrapping) their charges, resulting in a slow process that could happen for each trap state individually. If the trap environments overlap, collectively, i.e. the interaction between trap charges could amplify the effect of the external field. Since every relaxation process needs an anisotropy, it is much more likely that the interaction is between the same traps at different boundaries, i.e. a trap charge repositioning process (TCR) between boundaries [Luo et al 2013], instead of occurring between two groups of defects at the same boundary. In the TCR process, the trap charges go from one kind of boundaries (“fs” boundaries: perpendicular to E_{ext}) to another kind of boundaries (“fp” boundaries: parallel to E_{ext}) during the EC process, as shown in Fig. 4 (a). At the same time, the barrier layer (shown as the hand-drawn sign of peaks in Fig. 4(b)) constructed by trapped charges was gradually removed, then the I - V nonlinearity will change and the resistance will decrease monotonically, as shown in the inset of Fig. 1. However, in this process if only the barrier layers were repositioned, for a BLC model the recovery of the capacitance should not experience a peak. A dipole anisotropy of the trap levels should be considered along with the charge-only TCR processes. As shown in Fig. 4 (a), the ellipse sketches bipolar dipoles with two anisotropy axes (the major and minor axes). Assume that the dielectric polarisation is mainly determined by the orientation of such dipole moments, the accumulation and the arrangement of dipoles along the “fp” internal electric field will make the capacitance increase. However, when the dipoles will finally overcome the internal electric field and orientate to the external electric field, which will reduce the capacitance, thus we observe a capacitance peak.

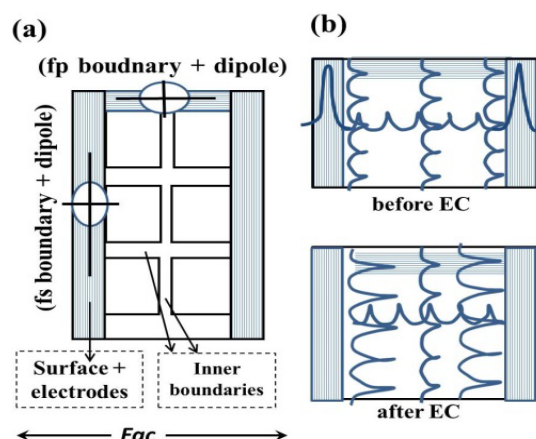


FIG. 4 (A) THE SKETCH OF THE SURFACE AND INTERGRAIN BOUNDARIES AND THEIR SCHOTTKY BARRIERS. THE ELLIPSE SKETCHES BIPOLAR DIPOLES WITH TWO ANISOTROPY AXES (THE MAJOR AND MINOR AXES) UNDER AN AC ELECTRIC FIELD E_{ac} . (B) THE BARRIER LAYER HEIGHT (SHOWN AS THE HAND-DRAWN SIGN OF PEAKS) CHANGES OF THE SURFACE AND INNER BOUNDARIES.

Conclusions

In sum, the electric field sensitivity of the semicircle III indicates (1) an unusually important role of the trap charges at the surface for the dielectric polarization, consistent with the still high dielectric response of single-crystal CCTO, and (2) the trap centers at the boundaries very likely develop an electrical dipole moment which contributes a major amount of the polarization.

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